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INFLUENCE OF ATMOSPHERIC CONDITIONS IN THE TESTING OF SUGARS

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That atmospheric conditions may exert an appreciable effect in the testing of sugar has been vaguely recognized for some years. The magnitude of this influence has, however, never been determined, and it is difficult to understand how this possible source of error has so long been practically ignored when we consider the large amount of research that has been carried on in an effort to reduce the process of testing to an exact science. Fortunately in the standardization of the saccharimeter, by means of the normal solution of sucrose, all chance of error from atmospheric conditions is eliminated. The normal weight of sucrose is made up to volume, and the polariscope tube is filled, under conditions that eliminate an appreciable change in the concentration of the unfiltered solution. In the process of testing, these conditions are unavoidably altered. The necessity for clarification requires that the liquid be passed once, and frequently twice, through ordinary filter paper to remove the precipitated impurities. While this is being done, there is more or less exposure to the atmosphere of the laboratory, with a consequent increase in the concentration. Since the rotation observed is directly proportional to the concentration, any change, if appreciable, must either be prevented or a correction applied to the polarization. Browne¹ and other investigators have recommended the use of cover glasses on the funnels to guard against possible evaporation.

The process of testing should obviously be such that when applied to the normal sucrose solution the polarization will be 100 on the saccharimeter scale within the limits of accuracy

¹ Browne: *Handbook of Sugar Analysis*, p. 205.

prescribed by other sources of error. With the object of accomplishing this, the suggestion has recently been made that the normal solution should be filtered in the determination of the 100° S point. Since atmospheric conditions vary greatly from day to day, such a procedure would be futile. On the other hand, the suggestion has been made that the 100° S point be set high. It has been shown by Bates and Jackson,² who have made an extended investigation of the 100° S point, the final results of which are now ready for publication, that the present basis of standardization of the saccharimeter is such that all near normal sugar solutions polarize approximately 0°:1 S too low; that is to say, the present 100° S point is approximately 0°:1 too high. In view of this fact, the suggestion has been made that the present value of the 100° point be left where it is, in order to allow for an increase of that magnitude in the polarization in ordinary testing, due to an increase in the concentration. This proposition, in our opinion, is untenable from a scientific standpoint, because it presupposes a constant effect of 0°:1 sugar, which is obviously not to be expected. The results of our investigation show that atmospheric conditions frequently introduce a relatively large error and that this error can always be eliminated.

The factors which influence the rate of evaporation from the surface of a liquid are numerous and the range of conditions under which this phenomenon occurs is so extensive that these factors may have a relatively wide variation in their magnitudes. In the greater part this accounts for the difficulty experienced by investigators, from the time of Dalton, in deriving a formula which adequately gives the rate of evaporation under all conditions in nature. Perhaps the most consistent formula is that of Marvin,³ which takes the following form:

$$\frac{dQ}{dt} = \frac{C}{B}(P_{as} + P_s - 2P_a)f(P)\varphi(V). \quad (1)$$

in which

dQ = quantity of water evaporated in time dt .

P = general symbol for vapor pressure.

² Orig. Com., 8th Int. Cong. of Applied Chemistry, 25, and Bureau of Standards Bulletin, 10.

³ Marvin: Monthly Weather Rev., February, 1909, 37:58, eq. 6.

P_s = saturation vapor pressure at temperature of water surface.

P_{as} = saturation vapor pressure at temperature of air near the water.

P_a = saturation vapor pressure at the temperature of the dew point in the air near the water.

B = barometric pressure.

V = velocity of wind.

C = constant.

Marvin states that the data available are as yet insufficient to evaluate the constant factors or to give the exact form of the terms depending on wind and atmospheric moisture. However, it is possible under certain conditions to solve (1) obtaining $\frac{dQ}{dt}$ with ample accuracy for special cases. In general the predomi-

nating variable factor in determining $\frac{dQ}{dt}$ is $(P_s - P_a)$, commonly designated the potential head. If we consider the special case of evaporation of water from a small vessel in the laboratory, a considerable simplification results. The influence of barometric pressure, as well as that of $f(P)$ and $\phi(V)$ becomes negligible; and $(P_{as} + P_s - 2P_a)$ reduces to $(P_s - P_a)$ under the permissible assumption that $P_{as} = P_a$; that is, that the air near the water surface is practically saturated at a temperature near the dew point, a condition roughly realized in the absence of ventilation.

The term $f(P)$ in (1) is somewhat indefinite. It was inserted by Marvin to provide for the contingency that under certain conditions the evaporation would not be strictly linear with the potential head. Just what form it might take is problematical. Fortunately, in our experiments, the conditions were such that it seemed probable that a straight-line relation would hold within the experimental errors of the observations. The experimental data given below fully sustain this conclusion.

We may then write

$$\frac{dQ}{dt} = CA(P_s - P_a) \quad (2)$$

or

$$Q = CA(P_s - P_a)T \quad (3)$$

where A is the area of the exposed surface. It will be observed that (2) and (3) cover the cases of zero and negative evaporation, the latter occurring when the temperature of the water is less than the temperature of the air at the dew point. We will show in what follows that (2) and (3) are directly applicable to the change in the concentration of the sugar solution, which ordinarily takes place in the testing of sugars.

METHODS USED

The area of the liquid from which evaporation can occur is constantly changing during the filtration. The total exposure is, however, the same for similar filtrations and the area, A , in equations (2) and (3) may consequently be taken as unity. If, then, we determine the constant C experimentally, we can calculate the evaporation for any potential head. Obviously, C may vary with the time of filtration, the rate of diffusion, the nature of the exposed surface, etc. It is nevertheless a constant for any particular set of similar filtrations.

We have utilized two methods for determining the change in concentration. The first tried was that of weighing the solution during filtration. The second, that of noting the change in the polarization. Since the polarization is directly proportional to the concentration, the change in polarization is proportional to the amount evaporated. $\frac{dQ}{dt}$ or more strictly, in the experiments, $\frac{Q}{T}$ thus has proportionate numerical values in both methods, provided the loss by evaporation is small as compared with the total quantity of solution. The loss in grams by weighing is equal to the increase in degrees sugar in the polarization. For convenience we have adopted the minute as the unit of time throughout our experiments.

In determining the potential head, P_a was calculated from the vapor-pressure tables for water, the necessary data being secured by means of the psychrometer referred to below. P_s is taken as the vapor pressure of water at the observed temperature of the solution. The lowering of the vapor pressure of the solution due to the presence of the sugar is negligible. At 30° C it amounts to 0.6 mm, which is equivalent to a change in the polarization of

0°.0006 sugar per minute. In all the experiments the normal solution—26 grams in 100 cc—was used.

APPARATUS

In order to carry out the experimental work it was found desirable to have control, during the filtration, of the atmospheric conditions over a wider range than would ordinarily occur in the average laboratory during a cycle of 12 consecutive months. This was made possible by the use of a constant temperature room with a content of about 15 cubic meters. The room was, in reality, a large thermostat, having a considerable range of accurate temperature adjustment. The air was kept thoroughly mixed by an electric fan which discharged over a false ceiling perforated with a large number of openings. Since equations (2) and (3) are based upon the elimination of the wind factor, (V), of equation (1), care was exercised to eliminate appreciable air currents. Tests with a sensitive anemometer showed this condition to be satisfactorily attained.

The moisture content of the air was regulated by freezing out some of the vapor by means of a brine coil or by admitting steam into the room, according as the amount of moisture present was greater or less than that desired.

The required temperature was maintained by an electric heater controlled by a mercury interrupter with a toluene coil, the maximum variations being about 0.3° C for any point between 15° C and 40° C. When once a given air condition had been secured it could be maintained indefinitely within satisfactory limits.

Any relative humidity between 17 per cent and 92 per cent could be attained at any temperature between 18° C and 39° C. Any desired potential head ($P_s - P_a$) could thus be obtained between 4 mm and 41 mm of mercury. An Assmann psychrometer was used for making all measurements of the amount of moisture.

The weighing experiments were made upon a large balance open to the atmosphere except while a weighing was being made, and sensitive to $\frac{1}{8}$ mg with a load of 200 g. The funnel and cylinder were placed directly upon the scale pan.

For making the polarization measurements, the Bates type of saccharimeter with adjustable sensibility was available. It was inclosed in a small thermostat, thus insuring a constant temperature during measurements. In order to secure a high degree of accuracy in the polarizations, the half-shadow angle was set at 3° . The light source was a Nernst lamp of 500 cp. The Bates type, 200 mm, metal polariscope tubes were used. The corrections for length were determined by the division of weights and measures of the Bureau of Standards. The glass funnels were stemless and had a diameter of 90 mm. The cylinders had a diameter of 40 mm and a height of 125 mm. The plaited type of filter with a diameter of 18.5 cm was used. Tests made on raw sugars when the smooth filters were employed gave results identical with those on the plaited type.

EXPERIMENTS WITH REFINED SUGAR

In the beginning of the work it was believed that the research could be satisfactorily consummated by the use of the best refined commercial sugar and that the results would be equally applicable to all sugars. This was desired because of the relative ease of manipulation and the avoidance of clarification.

The first experiments were made by the method of weighing. The solutions were made up at the temperature at which the tests were to be made. A clarifying reagent was not added. No cover was placed over the funnel. In order to retard the filtration so as to make the conditions comparable to those existing when raw sugars are tested, the bottom of the funnel was plugged with absorbent cotton. This effectually increased the time required for the solution to filter. In order to measure the total evaporation a solution was placed upon the pan of the balance and weighed at intervals of a few minutes until all had filtered through. The

average amount lost per minute, $\left(\frac{Q}{T}\right)$, by evaporation was then calculated. This was repeated for different conditions of temperature and humidity in order to secure data over a wide range of potential heads. Sufficient data was thus secured to solve equa-

tion (2) for the constant C . The results are given in Table 1. Taking the average of the values of C we have

$$\frac{Q}{T} = 0.0013 (P_s - P_a) \quad (4)$$

which gives the evaporation per minute under these conditions for any potential head. Column 6 gives the total loss in weight during the entire filtration. Columns 7 and 8 show the agreement between the observed evaporation and that calculated from equation (4). The results are shown graphically in Fig. 1.

TABLE 1

Refined Sugar; Funnel not Covered; Determinations by Weighing

$$\left[\frac{Q}{T} = 0.0013 (P_s - P_a) \right]$$

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|------------------------------|------------------------------|----------------------|-------------------------|-----------------|--|--|
| Tempera- ture of body of solution | Dry-bulb tempera- ture | Wet-bulb tempera- ture | Relative humidity | $P_s - P_a$ mm of Hg | Total change | Observed $\frac{Q}{T}$, grams per minute | Calculated $\frac{Q}{T}$, grams per minute |
| °C | °C | °C | Per cent | | g | | |
| 21.1 | 20.8 | 17.4 | 71.8 | 5.50 | 0.407 | 0.010 | 0.007 |
| 20.5 | 20.2 | 16.6 | 69.8 | 5.66 | 0.182 | 0.009 | 0.007 |
| 21.2 | 20.6 | 16.8 | 68.4 | 6.36 | 0.194 | 0.010 | 0.008 |
| 30.3 | 30.3 | 26.2 | 72.2 | 8.92 | 0.286 | 0.011 | 0.011 |
| 20.0 | 20.0 | 11.0 | 30.4 | 12.10 | 0.895 | 0.019 | 0.016 |
| 20.0 | 20.0 | 10.0 | 24.0 | 13.23 | 0.631 | 0.017 | 0.017 |
| 30.9 | 30.3 | 19.6 | 36.2 | 21.64 | 1.722 | 0.026 | 0.028 |
| 31.4 | 30.1 | 19.3 | 35.5 | 22.92 | 1.015 | 0.027 | 0.029 |
| 32.6 | 32.6 | 20.7 | 33.3 | 24.42 | 1.491 | 0.032 | 0.031 |
| 32.8 | 32.8 | 19.5 | 27.5 | 26.83 | 1.672 | 0.030 | 0.034 |

In order to secure sufficient clarification for polarizing a raw sugar it is frequently necessary to allow a portion, if not all the solution, to filter a second time. To find what portion of this total evaporation affects the solution which runs through and is used for polarization, tests were made on the saccharimeter. A tube was filled with the solution directly from the flask in which it was made up, thus obviating any loss by evaporation. Other solutions after being allowed to filter were polarized and com-

pared to the first tube as a point of reference. The difference in polarization between this tube and the other tubes is the effect due to evaporation during filtration. Careful experiments by weighing failed to show an appreciable evaporation while pouring the solution from the cylinder into the tube. Tables 2 and 3 show the effect of evaporation upon the polarization when the funnel is not covered. The time of filtration was about 12 minutes. It was hoped that the equations from this data would give the correction factors which would be applicable to raw sugars. Table 2 shows the increase in polarization for a single filtration, and we have

$$\frac{Q}{T} = 0.00066(P_s - P_a) \quad (5)$$

Table 3 shows the increase when the entire solution is filtered twice, and we have

$$\frac{Q}{T} = 0.00108(P_s - P_a) \quad (6)$$

The results are shown graphically in Fig. 1. It is surprising to find such a large increase per minute in the polarization when the solution is filtered twice.

TABLE 2

Refined Sugar; Funnel not Covered; Determinations by Polarization; Filtered Once

$$\left[\frac{Q}{T} = 0.00066 (P_s - P_a) \right]$$

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------|----------------------|----------------------|-------------------|------------------------|-----------------------------|--|--|
| Temperature of body of solution | Dry-bulb temperature | Wet-bulb temperature | Relative humidity | $P_s - P_a$, mm of Hg | Total change, degrees sugar | Observed $\frac{Q}{T}$, degrees sugar | Calculated $\frac{Q}{T}$, degrees sugar |
| ° C | ° C | ° C | Per cent | | | | |
| 30.4 | 30.4 | 27.9 | 82.6 | 5.65 | 0.08 | 0.007 | 0.004 |
| 20.0 | 20.0 | 12.4 | 40.0 | 10.45 | 0.03 | 0.006 | 0.007 |
| 19.9 | 19.9 | 11.2 | 32.6 | 11.66 | 0.16 | 0.009 | 0.008 |
| 32.0 | 33.0 | 23.0 | 42.4 | 19.49 | 0.25 | 0.014 | 0.013 |
| 34.0 | 36.6 | 19.2 | 17.2 | 31.72 | 0.24 | 0.017 | 0.021 |
| 35.1 | 36.2 | 18.8 | 16.7 | 34.61 | 0.30 | 0.023 | 0.023 |
| 36.0 | 37.9 | 20.1 | 19.5 | 35.62 | 0.18 | 0.025 | 0.024 |

TABLE 3

Refined Sugar; Funnel not Covered; Determinations by Polarization;
Filtered Twice

$$\left[\frac{Q}{T} = 0.00108 (P_s - P_a) \right]$$

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------|----------------------|----------------------|-------------------|------------------------|-----------------------------|--|--|
| Temperature of body of solution | Dry-bulb temperature | Wet-bulb temperature | Relative humidity | $P_s - P_a$, mm of Hg | Total change, degrees sugar | Observed $\frac{Q}{T}$, degrees sugar | Calculated $\frac{Q}{T}$, degrees sugar |
| ° C | ° C | ° C | Per cent | | | | |
| 30.4 | 30.4 | 27.9 | 82.6 | 5.65 | 0.11 | 0.003 | 0.006 |
| 20.0 | 20.0 | 12.4 | 40.0 | 10.45 | 0.22 | 0.011 | 0.011 |
| 19.9 | 19.9 | 11.2 | 32.6 | 11.66 | 0.35 | 0.013 | 0.013 |
| 32.0 | 33.0 | 23.0 | 42.4 | 19.49 | 0.43 | 0.019 | 0.021 |
| 35.1 | 36.2 | 18.8 | 16.7 | 34.61 | 0.50 | 0.038 | 0.037 |

Since equations (4), (5), and (6) show such large increases in the polarization, the experiments given in Tables 1 and 2 were repeated with the funnels covered with ordinary cover glasses, in order to determine how completely the evaporation could be prevented by this simple expedient. The results are given in Tables 4 and 5. In Table 4 the values in column 8 are calculated from equation (4) and in Table 5 from equation (6).

TABLE 4

Refined Sugar; Funnel Covered; Determinations by Weighing

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------|----------------------|----------------------|-------------------|-------------------------|--------------|---|--|
| Temperature of body of solution | Dry-bulb temperature | Wet-bulb temperature | Relative humidity | $P_s - P_a$, mm of Hg. | Total change | Observed $\frac{Q}{T}$, grams per minute | Calculated $\frac{Q}{T}$, grams per minute if not covered |
| ° C | ° C | ° C | Per cent | | g | | |
| 21.1 | 20.8 | 17.4 | 71.8 | 5.50 | 0.028 | 0.001 | 0.007 |
| 30.0 | 30.0 | 26.0 | 72.8 | 8.57 | 0.052 | 0.001 | 0.011 |
| 20.0 | 20.0 | 11.0 | 30.4 | 12.10 | 0.031 | 0.001 | 0.016 |
| 20.0 | 20.0 | 10.0 | 24.0 | 13.23 | 0.060 | 0.001 | 0.017 |
| 30.9 | 30.3 | 19.6 | 36.2 | 21.64 | 0.062 | 0.001 | 0.028 |
| 31.4 | 30.1 | 19.3 | 35.5 | 22.92 | 0.047 | 0.002 | 0.029 |
| 32.8 | 32.8 | 19.5 | 27.5 | 26.83 | 0.035 | 0.001 | 0.034 |

TABLE 5

Refined Sugar; Funnel Covered; Determinations made by Polarization;
Filtered Twice

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------------|------------------------------|------------------------------|----------------------|----------------------------|-------------------------------------|--|---|
| Temperature of body of solution | Dry-bulb tempera- ture | Wet-bulb tempera- ture | Relative humidity | $P_s - P_a$, mm of Hg. | Total change, de- grees sugar | Observed $\frac{Q}{T}$, degrees su- gar. | Calculated $\frac{Q}{T}$, if not covered, degrees su- gar. |
| ° C | ° C | ° C | Per cent | | | | |
| 20.0 | 20.0 | 12.4 | 40.0 | 10.45 | 0.00 | 0.000 | 0.007 |
| 20.0 | 20.0 | 10.2 | 25.3 | 13.01 | 0.02 | 0.001 | 0.014 |
| 20.0 | 20.0 | 10.2 | 25.3 | 13.01 | 0.06 | 0.002 | 0.014 |
| 20.0 | 20.0 | 10.2 | 25.3 | 13.01 | 0.03 | 0.000 | 0.014 |
| 20.0 | 20.0 | 10.2 | 25.3 | 13.01 | 0.03 | 0.001 | 0.014 |

It is evident from Tables 4 and 5 that the loss by evaporation, if the funnel is covered, is quite negligible, for all potential heads, amounting to only 0°.02 S for a filtration requiring 20 minutes. The object of the latter table was mainly to determine the agreement between the weighing and polarization methods. Four separate experiments were made at a potential head of 13 mm, in order to test the reproducibility of the polarization method.

EXPERIMENTS WITH RAW SUGAR

The experiments on refined sugar indicated the importance of making exhaustive tests on different grades of raw sugars to determine how far the preceding results could be applied to sugars requiring clarification. Three grades were used: Java, testing 97° S; Cuban, testing 94° to 95° S; and a very soft sugar, testing about 80° S. No appreciable differences in the evaporation were observed due to the grade of sugar. In every case 260 g was dissolved in water and the volume made up to 1000 cc at the temperature of the experiment. From 15 cc to 50 cc of basic lead acetate was added for clarification, the quantity used varying with the grade of sugar; 100-cc portions of the liquid were then used for the tests. The flask was thoroughly shaken before pouring off each portion, thus insuring a homogenous sample. To obtain a point of reference one filtration was always

made with the funnel covered. The change by evaporation from this sample was not greater than 0.02° S, as has been shown in Tables 4 and 5. Other portions of the solution were filtered without being covered and were compared to the reference tube. The results are given in Tables 6, 7, 8, and 9. The same method of tabulating the data has been used as in the tables for refined sugars. Since no difference in $\frac{Q}{T}$ was observed, due to the grade of the sugar, the values obtained for the three different grades have been incorporated into a single equation.

For the experiments in Table 6, the solutions were filtered once with the funnels uncovered, and we find

$$\frac{Q}{T} = 0.00017(P_s - P_a) \quad (7)$$

The results are shown graphically in Fig. 2.

TABLE 6

Raw Sugar; Funnel not Covered; Determinations by Polarization; Filtered Once

$$\left[\frac{Q}{T} = 0.00017(P_s - P_a) \right]$$

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------|----------------------|----------------------|-------------------|------------------------|-----------------------------|--|--|
| Temperature of body of solution | Dry-bulb temperature | Wet-bulb temperature | Relative humidity | $P_s - P_a$, mm of Hg | Total change, degrees sugar | Observed $\frac{Q}{T}$, degrees sugar | Calculated $\frac{Q}{T}$, degrees sugar |
| $^{\circ}\text{C}$ | $^{\circ}\text{C}$ | $^{\circ}\text{C}$ | Per cent | | | | |
| 27.8 | 28.0 | 25.3 | 80.0 | 4.21 | 0.02 | 0.001 | 0.001 |
| 27.5 | 27.6 | 24.8 | 79.8 | 5.42 | 0.04 | 0.002 | 0.001 |
| 24.1 | 24.1 | 14.0 | 30.9 | 15.42 | 0.12 | 0.005 | 0.003 |
| 24.8 | 24.8 | 14.1 | 28.4 | 16.66 | 0.03 | 0.003 | 0.003 |
| 25.0 | 25.1 | 13.9 | 26.5 | 17.29 | 0.06 | 0.006 | 0.003 |
| 28.4 | 27.3 | 15.8 | 28.2 | 21.18 | 0.02 | 0.001 | 0.004 |
| 30.4 | 27.3 | 15.8 | 28.2 | 24.70 | 0.11 | 0.005 | 0.004 |
| 34.0 | 36.9 | 19.2 | 16.5 | 31.92 | 0.10 | 0.006 | 0.006 |
| 37.4 | 39.0 | 20.7 | 17.2 | 38.79 | 0.05 | 0.004 | 0.007 |
| 38.4 | 39.1 | 20.9 | 17.8 | 41.16 | 0.08 | 0.007 | 0.007 |
| 38.4 | 39.1 | 20.9 | 17.8 | 41.16 | 0.11 | 0.008 | 0.007 |

For Table 7 the solutions were poured back when one-half had filtered. The funnels were not covered. We then have—

$$\frac{Q}{T} = 0.00049(P_s - P_a) \quad 8$$

The results are shown graphically in Fig. 2.

TABLE 7

Raw Sugar; Funnel not Covered; Determination by Polarization; Solution
Poured Back When One-Half Filtered

$$\left[\frac{Q}{T} = 0.00049(P_s - P_a) \right]$$

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------------|------------------------------|------------------------------|----------------------|------------------------------|--------------------------------------|---|---|
| Temperature of body of solution | Dry-bulb tempera- ture | Wet-bulb tempera- ture | Relative humidity | $P_s - P_a$, mm of Hg | Total change, degrees sugar | Observed $\frac{Q}{T}$, degrees sugar | Calculated $\frac{Q}{T}$, degrees sugar |
| ° C | ° C | ° C | Per cent | | | | |
| 27.8 | 28.0 | 25.3 | 80.0 | 4.21 | 0.05 | 0.002 | 0.002 |
| 27.5 | 27.6 | 24.8 | 79.8 | 5.42 | 0.03 | 0.001 | 0.003 |
| 24.6 | 24.6 | 14.8 | 33.0 | 15.32 | 0.20 | 0.005 | 0.007 |
| 24.8 | 24.8 | 14.1 | 28.4 | 16.66 | 0.22 | 0.011 | 0.008 |
| 25.0 | 25.1 | 13.9 | 26.5 | 17.29 | 0.25 | 0.013 | 0.008 |
| 28.4 | 27.3 | 15.8 | 28.2 | 21.18 | 0.22 | 0.010 | 0.010 |
| 30.4 | 27.3 | 15.8 | 28.2 | 24.70 | 0.46 | 0.013 | 0.012 |
| 34.0 | 36.9 | 19.2 | 16.5 | 31.92 | 0.62 | 0.023 | 0.016 |
| 37.4 | 39.0 | 20.7 | 17.2 | 38.79 | 0.23 | 0.012 | 0.019 |
| 38.4 | 39.1 | 20.9 | 17.8 | 41.16 | 0.30 | 0.022 | 0.020 |
| 38.4 | 39.1 | 20.9 | 17.8 | 41.16 | 0.34 | 0.017 | 0.020 |

For Table 8 the solutions were filtered twice with the funnels uncovered. We have—

$$\frac{Q}{T} = 0.00070(P_s - P_a) \quad 9$$

The results are shown graphically in Fig. 2.

TABLE 8

Raw Sugar; Funnel not Covered; Determination by Polarization; Filtered Twice

$$\left[\frac{Q}{T} = 0.00070(P_s - P_a) \right]$$

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------|----------------------|----------------------|-------------------|------------------------|-----------------------------|--|--|
| Temperature of body of solution | Dry-bulb temperature | Wet-bulb temperature | Relative humidity | $P_s - P_a$, mm of Hg | Total change, degrees sugar | Observed $\frac{Q}{T}$, degrees sugar | Calculated $\frac{Q}{T}$, degrees sugar |
| ° C | ° C | ° C | Per cent | | | | |
| 27.8 | 28.0 | 25.3 | 80.0 | 4.21 | 0.17 | 0.005 | 0.003 |
| 27.5 | 27.6 | 24.8 | 79.8 | 5.42 | 0.20 | 0.005 | 0.004 |
| 24.1 | 24.1 | 14.0 | 30.9 | 15.42 | 0.45 | 0.011 | 0.011 |
| 28.4 | 27.3 | 15.8 | 28.2 | 21.18 | 0.55 | 0.016 | 0.015 |
| 30.4 | 27.3 | 15.8 | 28.2 | 24.70 | 0.84 | 0.018 | 0.017 |
| 34.0 | 36.9 | 19.2 | 16.5 | 31.92 | 1.16 | 0.023 | 0.022 |
| 37.4 | 39.0 | 20.7 | 17.2 | 38.79 | 0.78 | 0.026 | 0.027 |
| 38.4 | 39.1 | 20.9 | 17.8 | 41.16 | 0.78 | 0.029 | 0.029 |
| 38.4 | 39.1 | 20.9 | 17.8 | 41.16 | 0.68 | 0.023 | 0.029 |

In Table 9 the funnels were covered. A point of reference was secured by allowing a sample to filter once, since it was impossible to polarize without filtration. For the other tests the solution was poured back on the filter when (a) about one-half had run through; (b) all had run through. The cover was removed from the funnel while the solution was being poured back and was then immediately replaced.

Column 8 was calculated from equations (8) and (9).

TABLE 9

Raw Sugars; Funnels Covered; Determination by Polarization.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------|----------------------|----------------------|-------------------|------------------------|-----------------------------|--|--|
| Temperature of body of solution | Dry-bulb temperature | Wet-bulb temperature | Relative humidity | $P_s - P_a$, mm of Hg | Total change, degrees sugar | Observed $\frac{Q}{T}$, degrees sugar | Calculated $\frac{Q}{T}$, if not covered, degrees sugar |
| °C | °C | °C | Per cent | | | | |
| 24.6 | 24.6 | 14.8 | 33.0 | 15.32 | 0.000 | 0.000 | ⁴ 0.008 |
| 24.6 | 24.6 | 14.8 | 33.0 | 15.32 | 0.015 | 0.001 | ⁴ 0.008 |
| 24.6 | 24.6 | 14.8 | 33.0 | 15.32 | -0.025 | -0.001 | ⁵ +0.010 |
| 24.6 | 24.6 | 14.8 | 33.0 | 15.32 | 0.020 | 0.001 | ⁵ 0.010 |

⁴ Poured back when half through.

⁵ Poured back when all through.

DISCUSSION OF RESULTS

In the preceding experiments $\frac{Q}{T}$ has been measured for potential heads as high as 41 mm of mercury. During the summer months, when it is most likely to be a maximum, the potential head rarely exceeds 22 mm and is usually much lower; 22 mm corresponds roughly to a temperature of 30° and a relative humidity of 30 per cent. $\frac{Q}{T}$ for the curve obtained by weighing is much larger than the corresponding value obtained by the polarization method. (See Fig. 1.) This probably is caused by the evaporation from the solution that remains on the filter and which produces no increase in the concentration of the solution which passes the filter. The method of weighing determines the total evaporation, whereas not all the evaporation is instrumental in raising the polarization when that method is utilized.

The curves in Fig. 2 show at a glance how inapplicable the corrections for refined sugar are to raw sugars. $\frac{Q}{T}$ for the once filtered solution is surprisingly small when compared with the similar curve in Fig. 1. Certainly evaporation from a solution containing a precipitate is much slower than from one containing none. We believe that this phenomenon, because of its direct effects on many laboratory operations, should receive further study.

When the solution is filtered but once, the increase in the polarization (see Fig. 2) for a potential head of 22 mm and a filtration of 10 minutes duration, is less than 0°.04 S. The conclusion, therefore, is reached that it is unnecessary, in the ordinary testing of raw sugars, to use any precautions to prevent or to correct for evaporation, provided that it is not necessary to pour any portion of the filtrate back on the filter. All the more unexpected, then, is the large increase in $\frac{Q}{T}$, as shown by the curves in Fig. 2, when a part or all of the solution is filtered a second time. After careful consideration we have concluded that this is caused largely by the solution which is returned to the filter taking up the solution

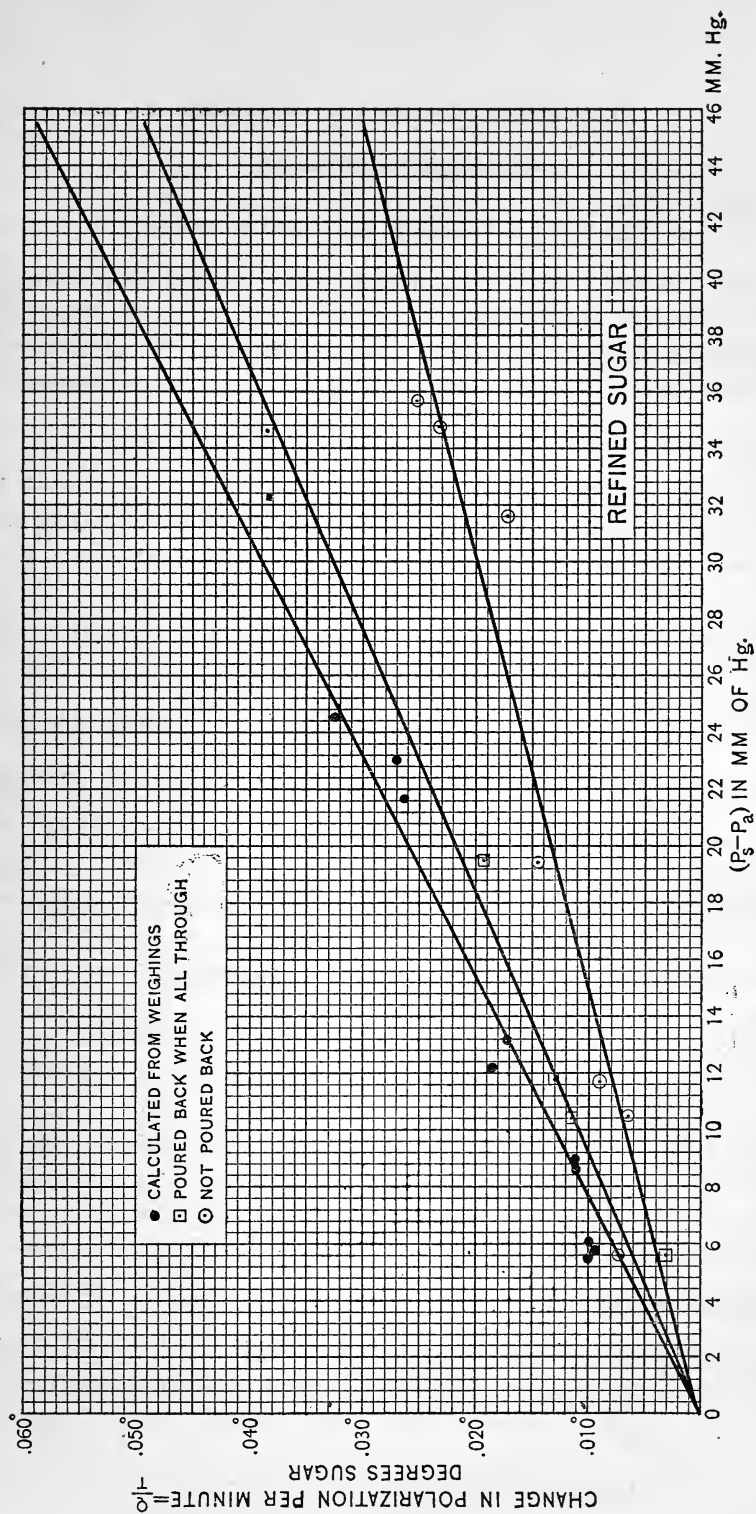


Fig. 1.

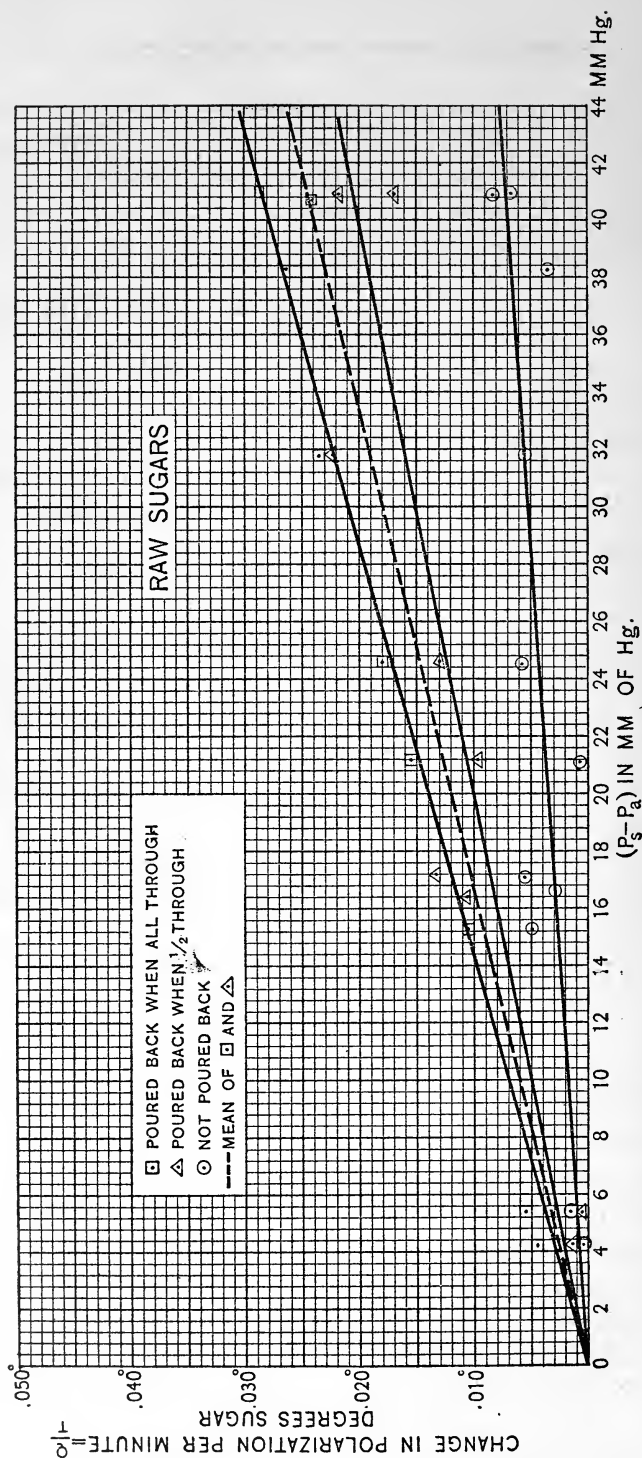


Fig. 2.

already adhering to the filter and which has become concentrated by evaporation after the level of the solution in the funnel has fallen. It thus becomes imperative in this case either to prevent evaporation or to apply a correction to the polarization. The correction may most conveniently be taken from the broken

curve $\frac{Q}{T} = 0.00060 (P_s - P_a)$, which is the mean of the curve for

solutions poured back when one-half has filtered, and the curve for solutions twice filtered. (See Fig. 2.)

Since the practice of returning at least a part of the first filtrate to an uncovered filter is quite general, the conclusion is unavoidable that in many laboratories tests are frequently in error by several tenths of a sugar degree. The important influence of atmospheric conditions on sugar tests has remained so long undetermined, probably because polarizations made on the same sugar and compared with one another are usually made at the same time and hence under similar potential heads. The results, therefore, agree among themselves, although relatively large errors may be present. The importance of either eliminating or correcting for the evaporation when tests made in different laboratories are to be compared can not be overestimated.

Tables 4, 5, and 9 show that for most purposes any increase in the polarization may effectively be prevented by covering the funnel during the filtration. In laboratories where a large number of tests are made daily this is somewhat of a burden, but it is generally a simpler procedure than making the correction for the potential head.

Owing to the importance, for scientific and commercial purposes, of the 100° S point on the saccharimeter, it is desirable that this point be determined with the highest obtainable precision. Especially prepared sucrose is used, and the solution is not only unfiltered, but it is also protected from any change in concentration while being transferred from the flask to the polarization tube. This procedure is necessary in order to obtain a result that is accurately reproducible. It is surprising that in view of the dissimilarity between the method for testing raw sugars and the procedure in determining the 100° S point that the effects of changes

in concentration have not been carefully studied. It has long been recognized that the ideal conditions of having both procedures identical is not practicable. The possibility of errors has always been admitted, but owing to the lack of accurate data on the subject the matter has been generally ignored. Unfortunately, the uncertainty thus introduced has been used at times as an argument against a revision of the 100° S point, the statement being made that it was not necessary to know the 100° S point accurately, because of the possible errors in the polarization of a sugar, due to changes in concentration. The results of the present investigation would seem to eliminate from consideration this argument against an accurate revision of the 100° S point of the saccharimeter.

As a result of the conclusions which have been drawn from the preceding data we would suggest the following for the guidance of those who desire to secure the true polarizations of raw sugars:

RAW SUGAR, FILTERED ONCE

1. The increase in the polarization due to evaporation is negligible in ordinary testing for all potential heads up to 22 mm and it is therefore unnecessary to use any precautions to prevent or to correct for evaporation for ordinary atmospheric conditions, provided the duration of the filtration does not exceed 10 or 12 minutes.

2. If the correction for the increase in polarization is desired, it may be obtained from

$$Q = 0.00017 (P_s - P_a) T \quad (10)$$

where Q = increase in polarization in degrees sugar.

P_s = saturation vapor pressure at the temperature of the solution.

P_a = saturation vapor pressure at the temperature of the dew point in the air.

T = time of filtration, in minutes.

Q should be subtracted from the observed polarization to obtain the true polarization.

3. Practically all increase in polarization, regardless of atmospheric conditions, may be prevented by covering the funnel with a watch glass.

RAW SUGAR; NOT LESS THAN ONE-FOURTH OF SOLUTION FILTERED TWICE

4. The increase in the polarization due to evaporation is not negligible in ordinary testing, but may amount to several tenths of a sugar degree. It is therefore necessary to prevent or to correct for evaporation for ordinary atmospheric conditions.

5. The correction for the increase in the polarization may be calculated from

$$Q = 0.00060 (P_s - P_a) T \quad (11)$$

where Q , P_s , P_a , and T have the definitions given in 2. Q should be subtracted from the observed polarization to obtain the true polarization.

6. Practically all increase in polarization, regardless of atmospheric conditions, may be prevented by covering the funnel with a watch glass.

WASHINGTON, February 1, 1914.

